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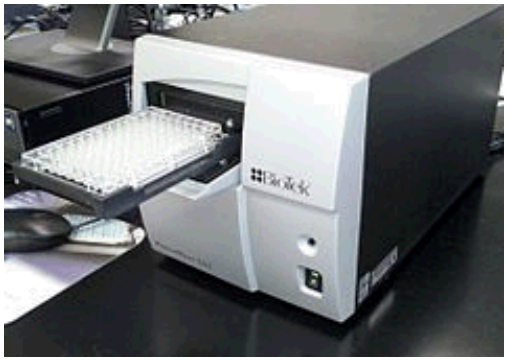

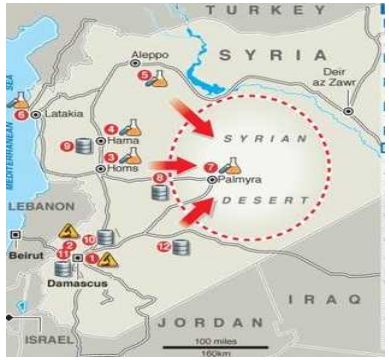

Combinatorial, Microscale Fuel/Oxidizer Formulations for the Systematic Determination of Homemade Explosives Properties

Christina L. Beppler

2015 Trace Explosives Detection Workshop

Pittsburgh, PA, April 27-May 1, 2015

U.S. DEPARTMENT OF ENERGY | NNSA National Nuclear Security Administration

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Advanced HME Formulation

- We are investigating new and innovative ways to *formulate* (not synthesize) HMEs – both in order to streamline R&D and to understand potential emerging threats
  - Combinatorial HME formulation with an inkjet printer
    - Developing a *capability* to rapidly print various HME formulations (starting with binary fuel/oxidizer mixtures) for use in research and detection understanding
    - Develop an *analytical workflow framework* that can be applied to emerging threats to streamline sample analysis
    - Research spans deposition work, chemical and physical data collection, and data analysis and organization

Potassium chlorate

1/1 PC/sucrose

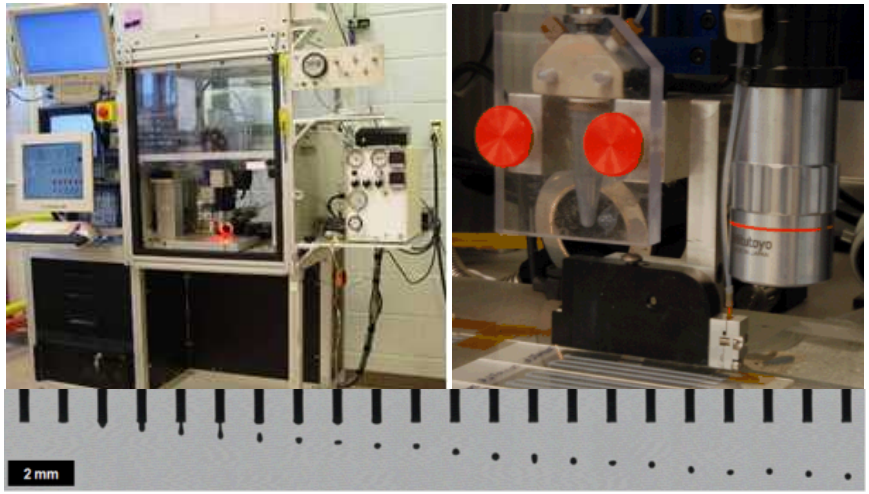
Sucrose

Combinatorial HME Formulation

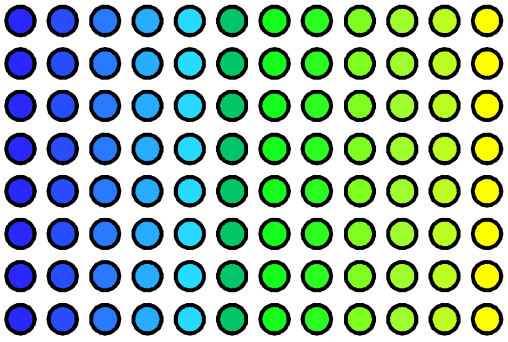
- For all intents and purposes, homemade explosives are used for nefarious reasons
- Little work on systematically studying physical and chemical properties of HMEs to determine how to best detect / identify them
  - Too many combinations and permutations, ratios and impurities – time and expense
  - Safety concerns considering the amounts that are usually made
- We are looking at formulating HMEs in small quantities using inkjet printing
  - Individual samples that are <10 mg arrayed in 48 and 96-well plates (industry standard)
  - Use standard analytical instrumentation (DSC/TGA, Mass Spec, IC, Raman) to identify components of each HME and differences between them
  - Investigate novel ways to store and analyze the data to aid in decision making processes
- Creating a capability that can rapidly, safely, and inexpensively characterize existing and new threats to aid in their detection and attribution
  - Understand the extent to which bulk-scale HME formulations can be approximated with microscale formulations
  - Collect a range of data on known, current binary fuel/oxidizer threats
  - Create a data analysis approach that allows for thoughtful and rapid decision making
  - Create a capability architecture that can be expanded to other materials or more complex threats as needed – the method will lend itself to increased complexity/scale up

Inkjet Printing of HME Formulations

Inkjet Printer Deposition



96 well plate



Fuel *Mixtures* *Oxidizer*

HMEs already printed into sample pans/containers

Characterization

- **Environmental Aging (temperature, humidity, time)**
- **Chromatography (ion, liquid, gas)**
- **Differential Scanning Calorimetry / Thermogravimetric Analysis**
- **Mass Spectrometry**
- **Scanning Raman Spectroscopy**

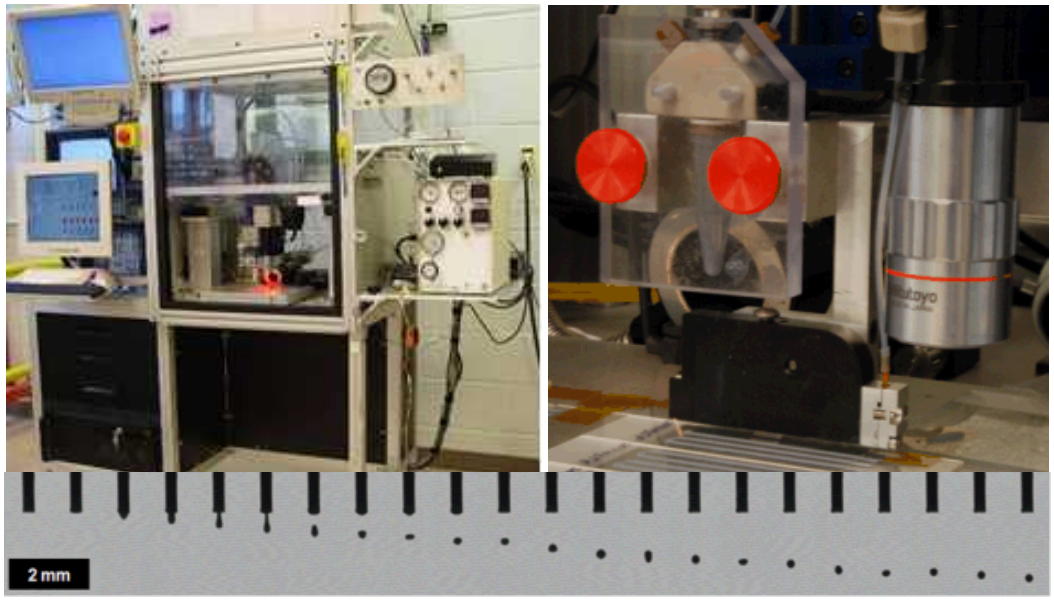
Data

- **Vapor Pressures**
- **Impurities, Degradation Products**
- **Material lifetimes**

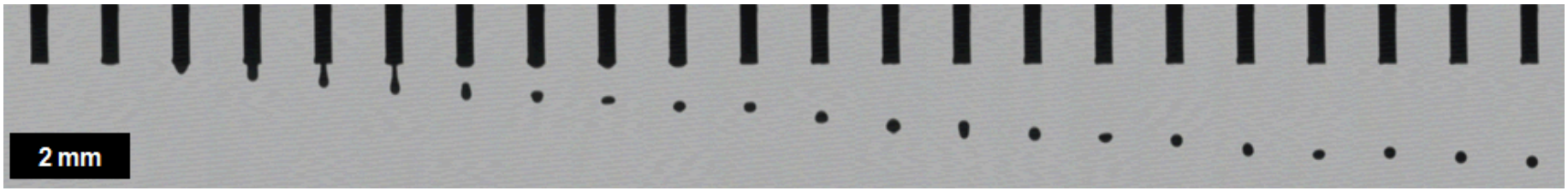
Actionable Knowledge to aid in detection efforts

Inkjet Printing System

- Three-axis positioning system
- Microscopes for droplet imaging and registration
- PipeJet™ dispensing mechanism
  - Dosage volumes range from a few nanoliters to several microliters per second
  - Volume dispensed is independent of the liquid's properties like viscosity or surface tension over a wide range
  - Particle laden dispersions can be easily printed – clogging is limited



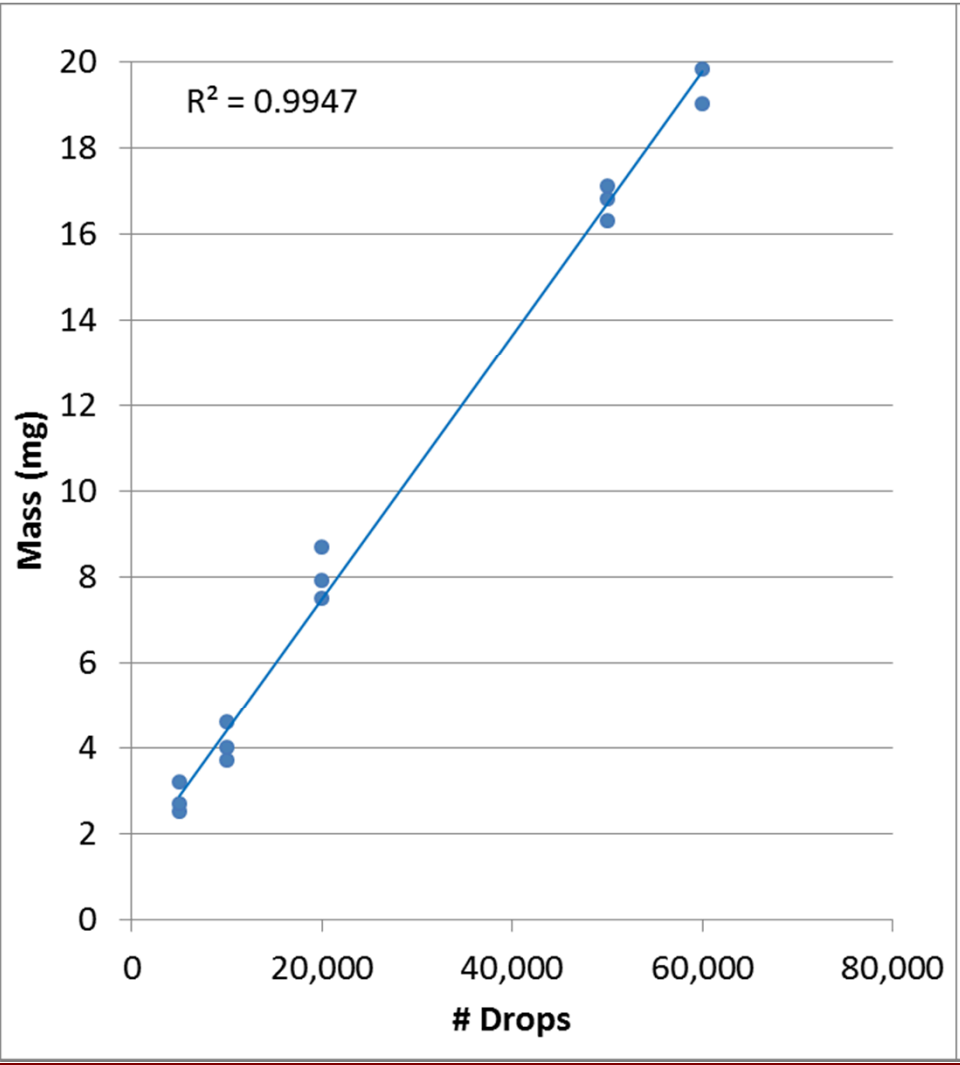
Inkjet dispensing system showing reservoir, dispensing tip, and registration microscope.



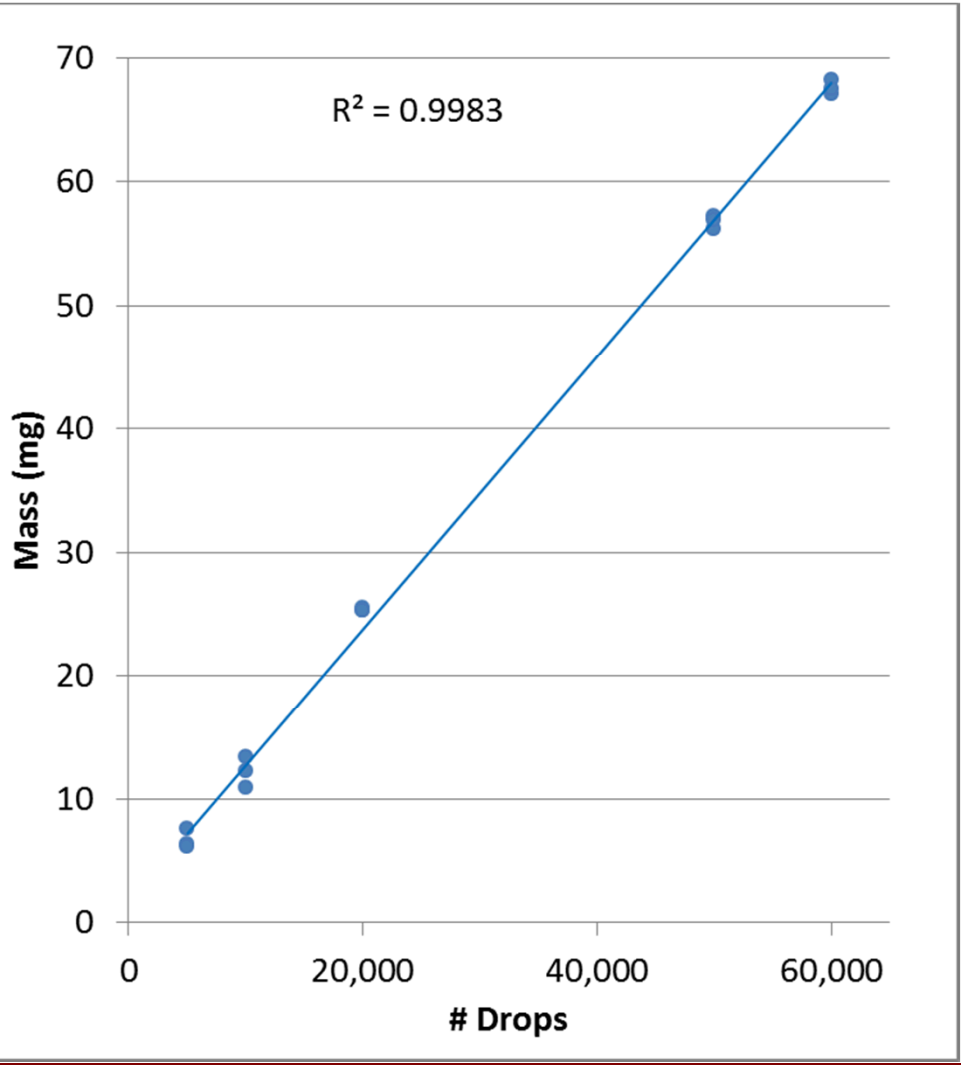
Strobe-illuminated photographs of Al/Bi_2O_3 ink droplet formation. 100 µs between images.

Calibration Printing – PC and AN

25 mg/mL potassium chlorate in water

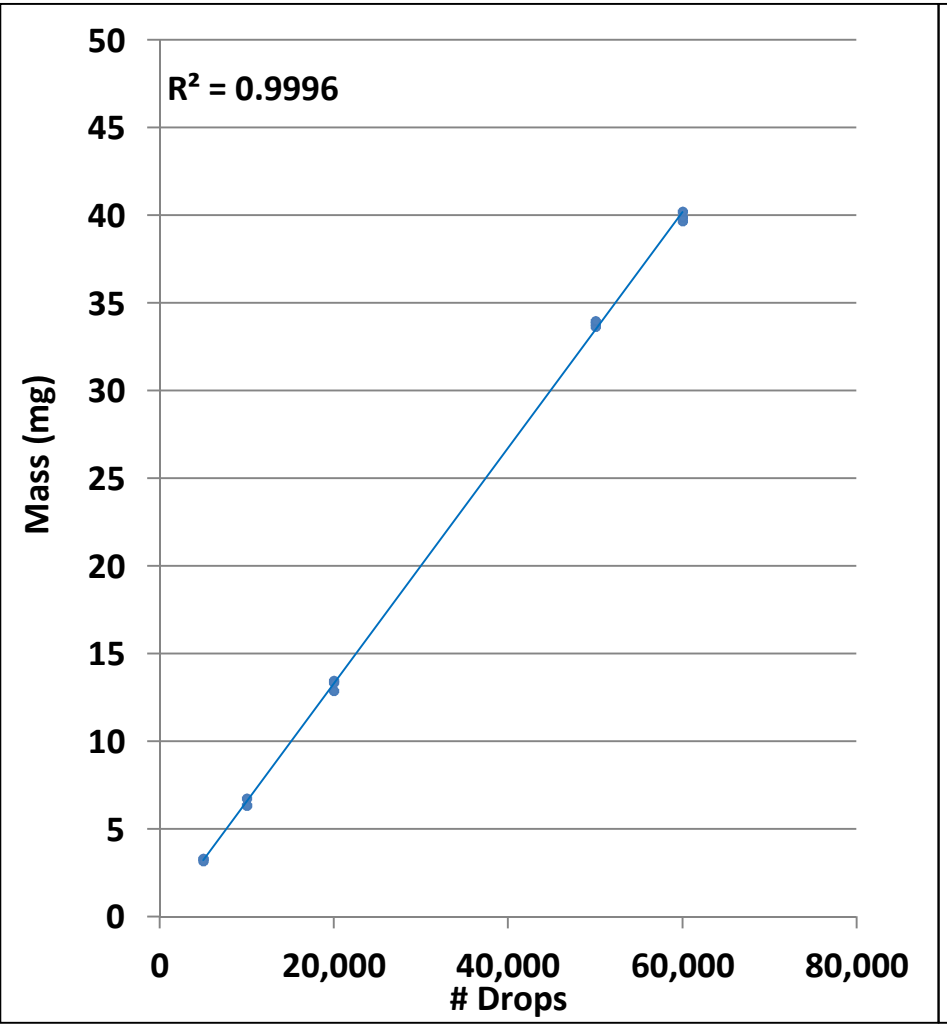


100 mg/mL ammonium nitrate in water

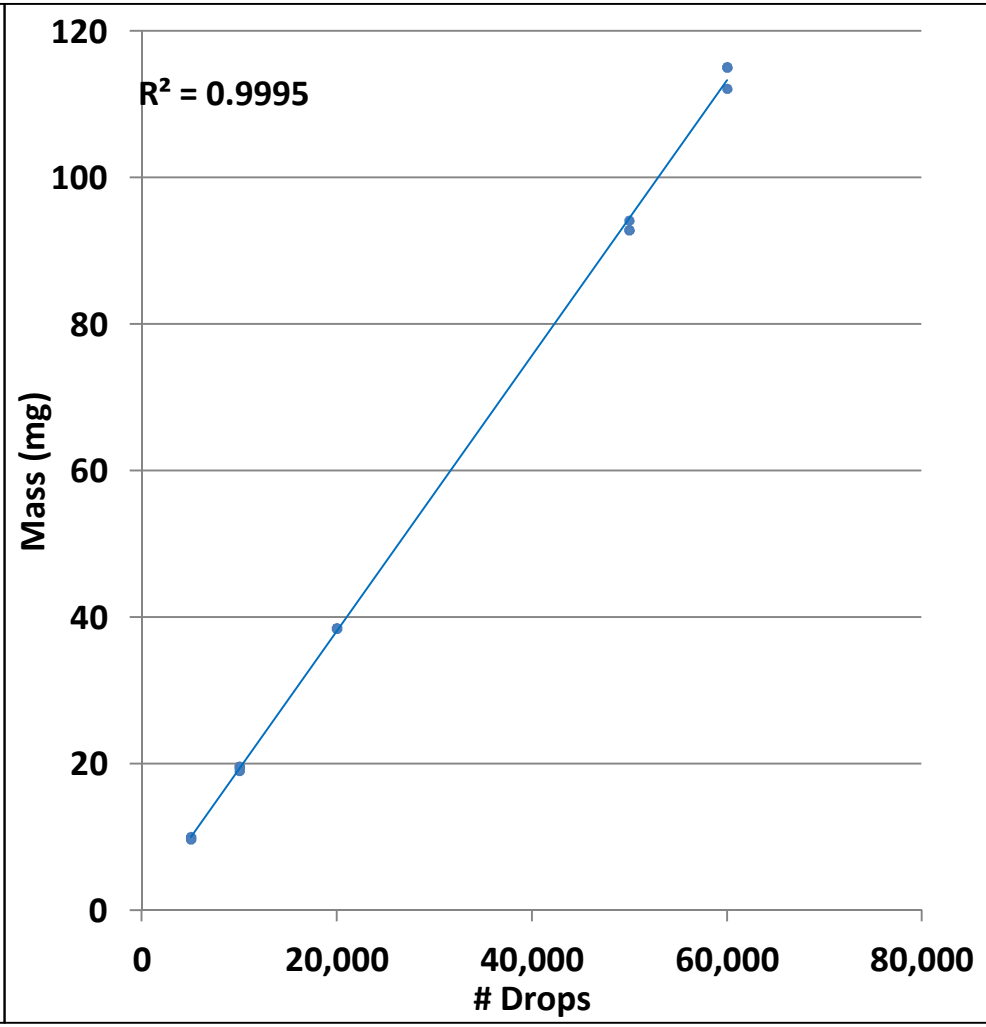


Calibration Printing - Sucrose

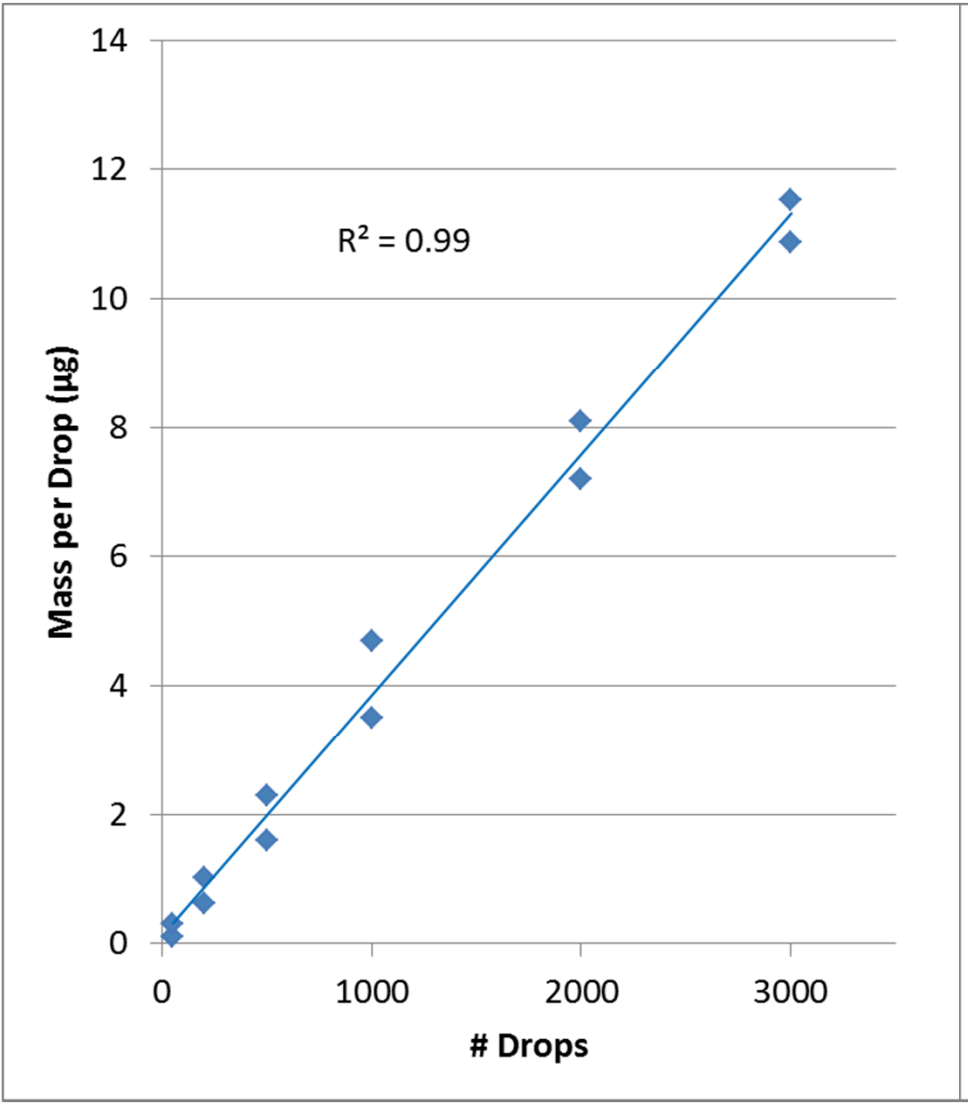
50 mg/mL sucrose in water

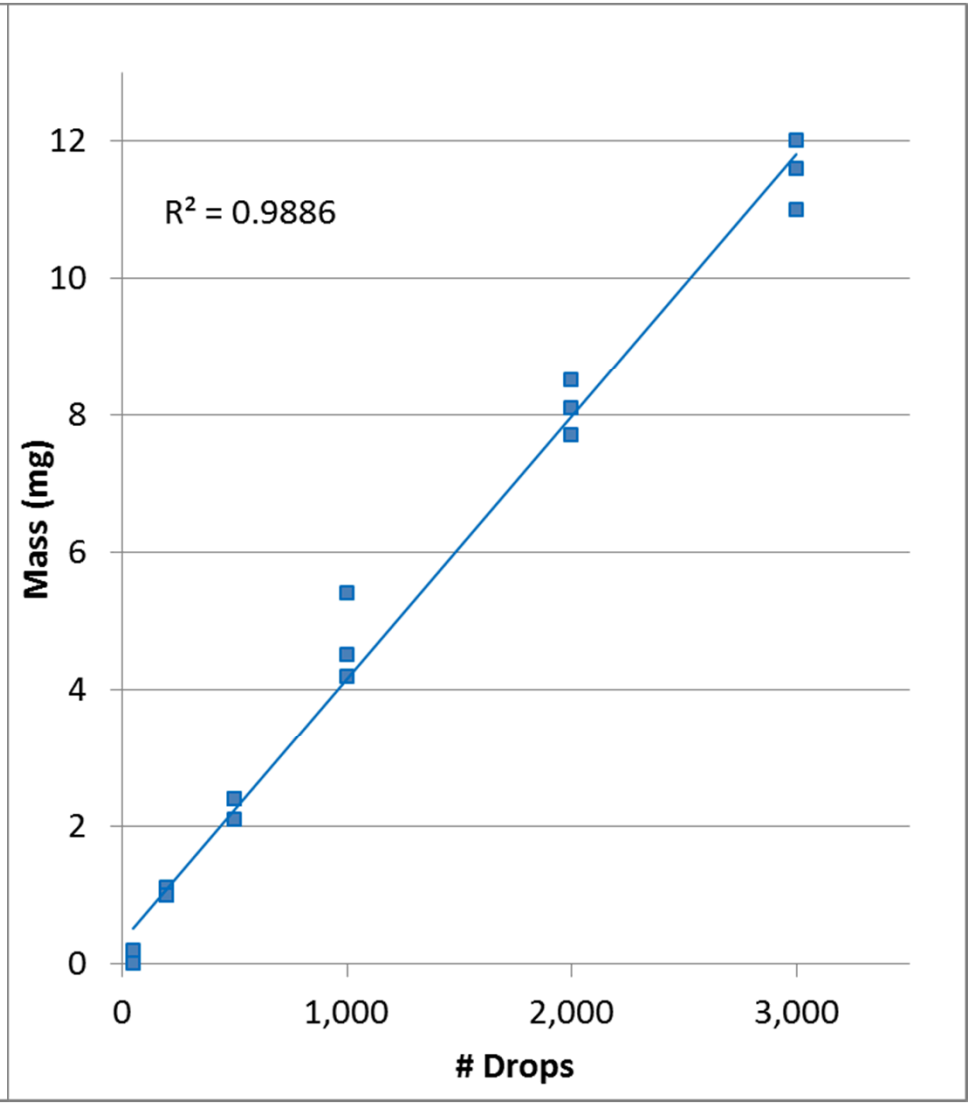


200 mg/mL sucrose in water



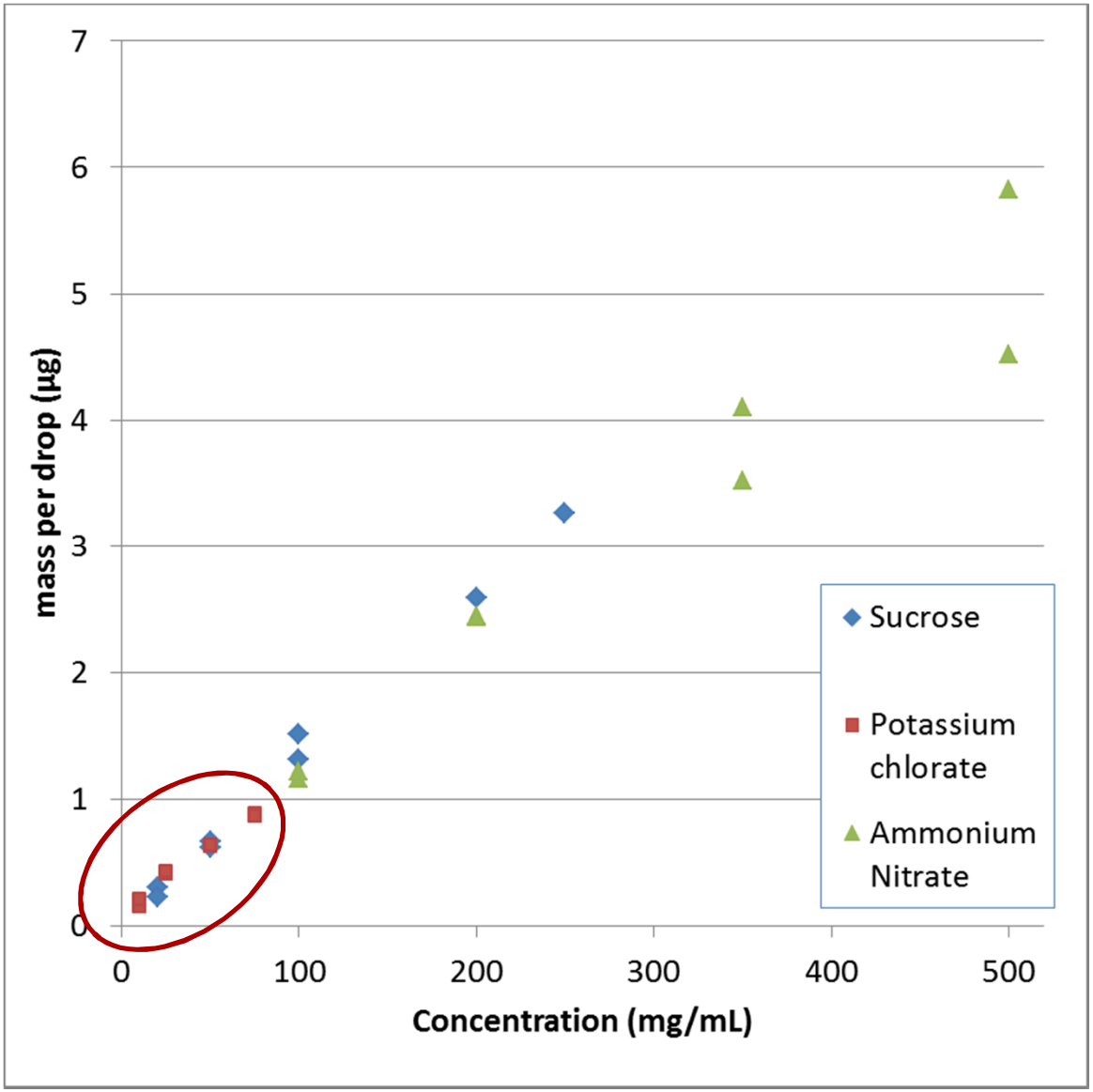
Pure Dodecane Deposition





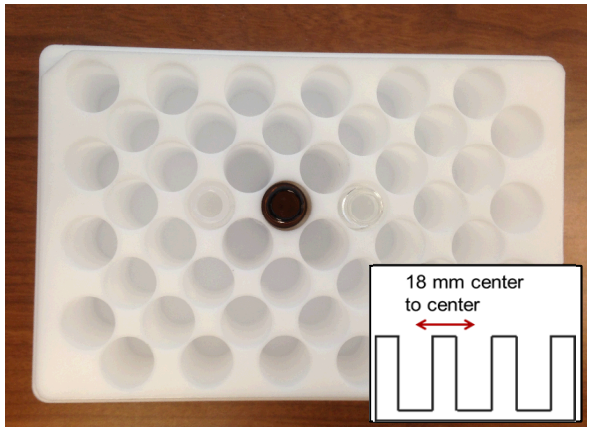
All Calibration Data

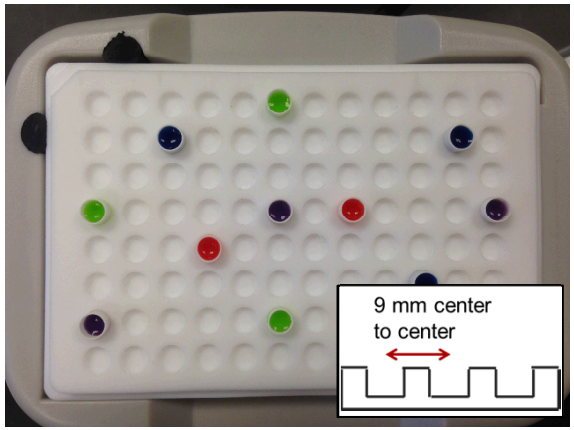
- Visualizing all the data together shows the target concentration regime
- Concentration regime allows for printing the same number of drops for each material
- Need to factor in:
  - required deposited amounts (1-10 mg total per well)
  - Volumes dispensed (not to overflow wells/containers
  - Printing process parameters
- Staying within the 10 – 80 mg mL^{-1} concentration regime seems to be the best option, ideally choosing one concentration for all materials

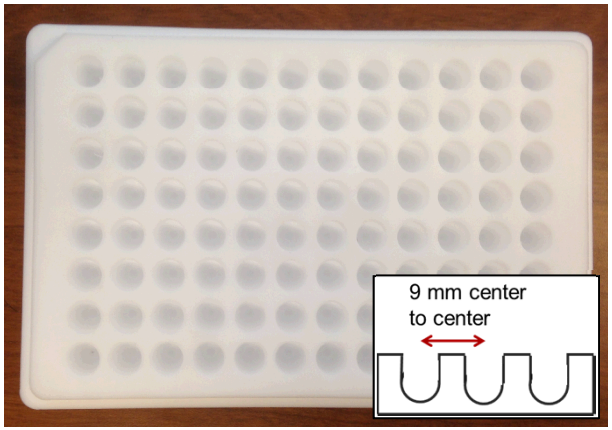


Customized Well Plates

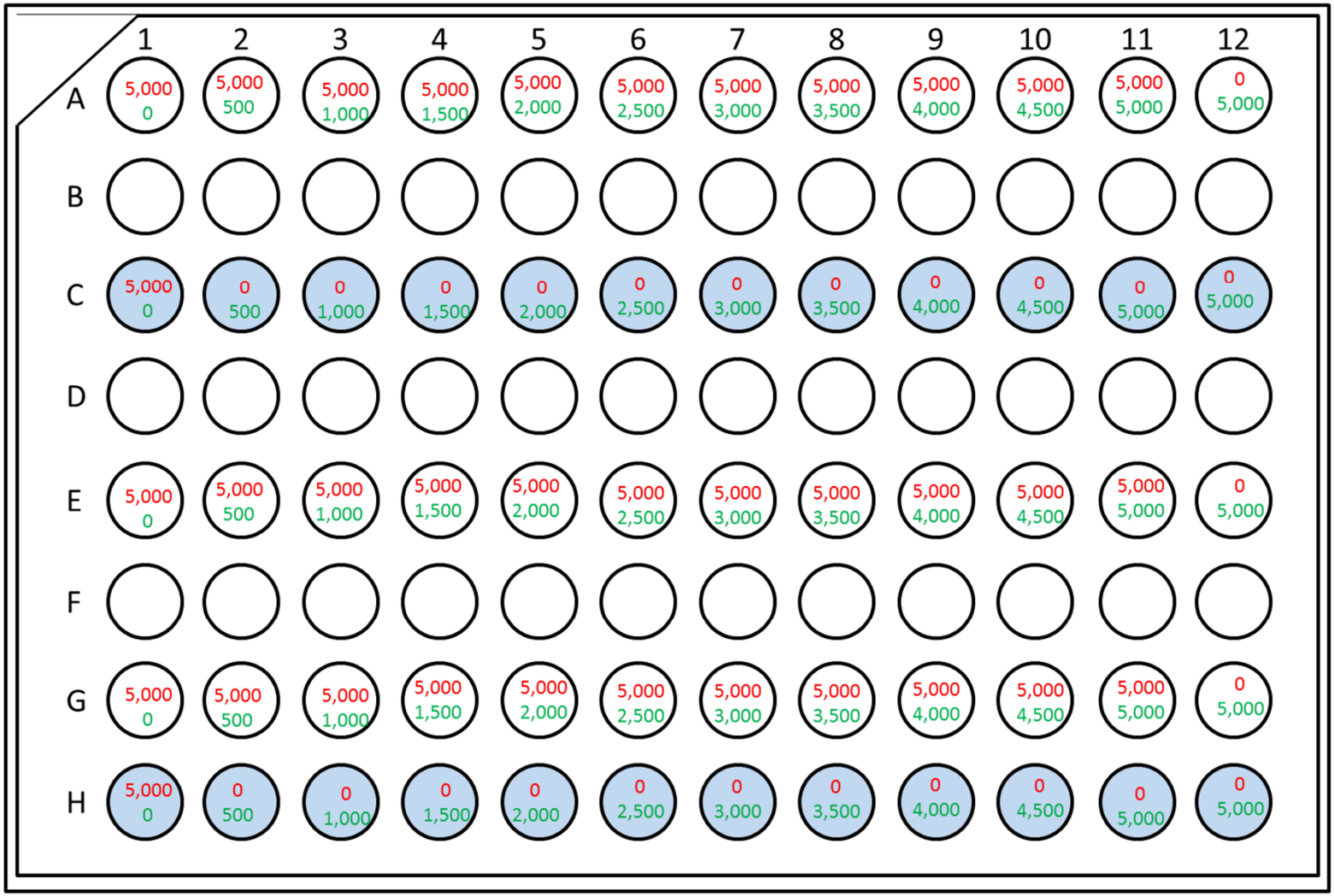
- Industry standard 96-well plates are attractive for throughput and standardization
- Eventually can print directly into well plates for a given instrument and analyze in an automated fashion for high throughput
- Large number of samples allows for proper statistics and confidence in results
- For R&D purposes we are using custom-made well plates (PTFE) with same overall dimensions and spacing as ANSI industry standard (9 mm center to center distances, 18 mm for vial-containing 48-well plates)
- Well plates designed for holding containers are designed to have container protrude for easy insertion/removal and potential sealing during aging





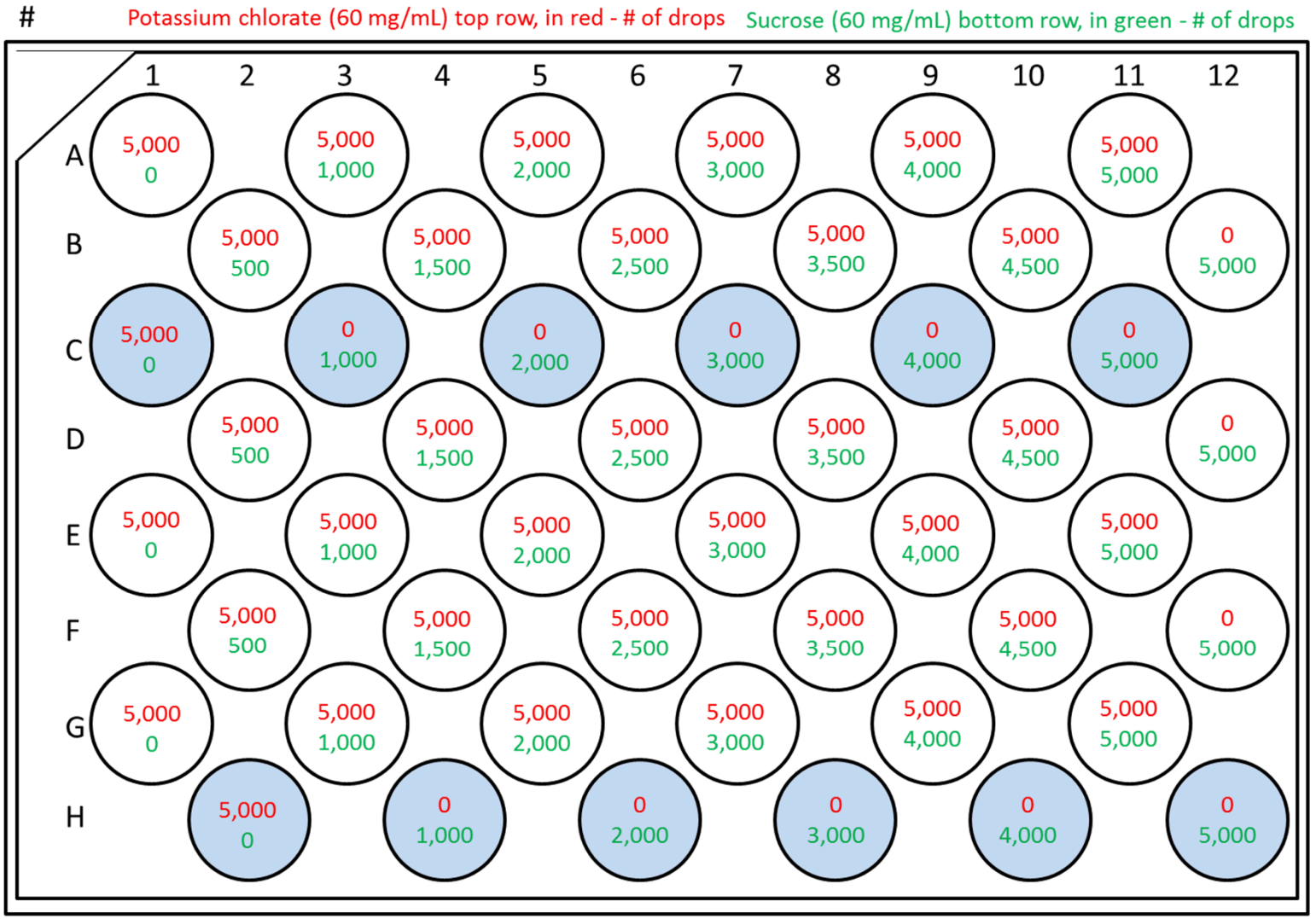


96-Well Plates- Example



Notes: 500 drop increments, alternating inks. Shaded wells are for calibrations

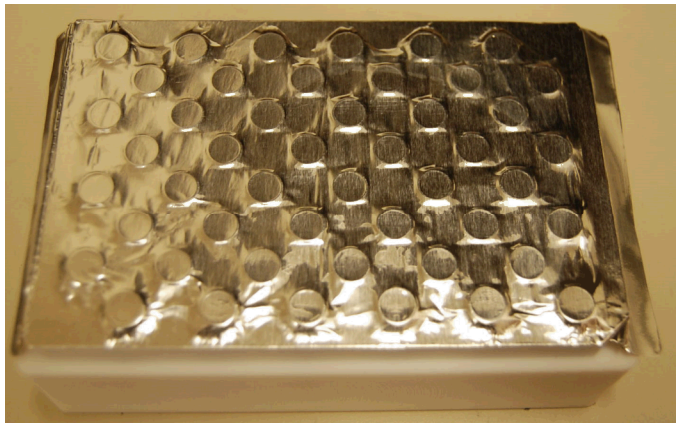
48-Well Plates - Example

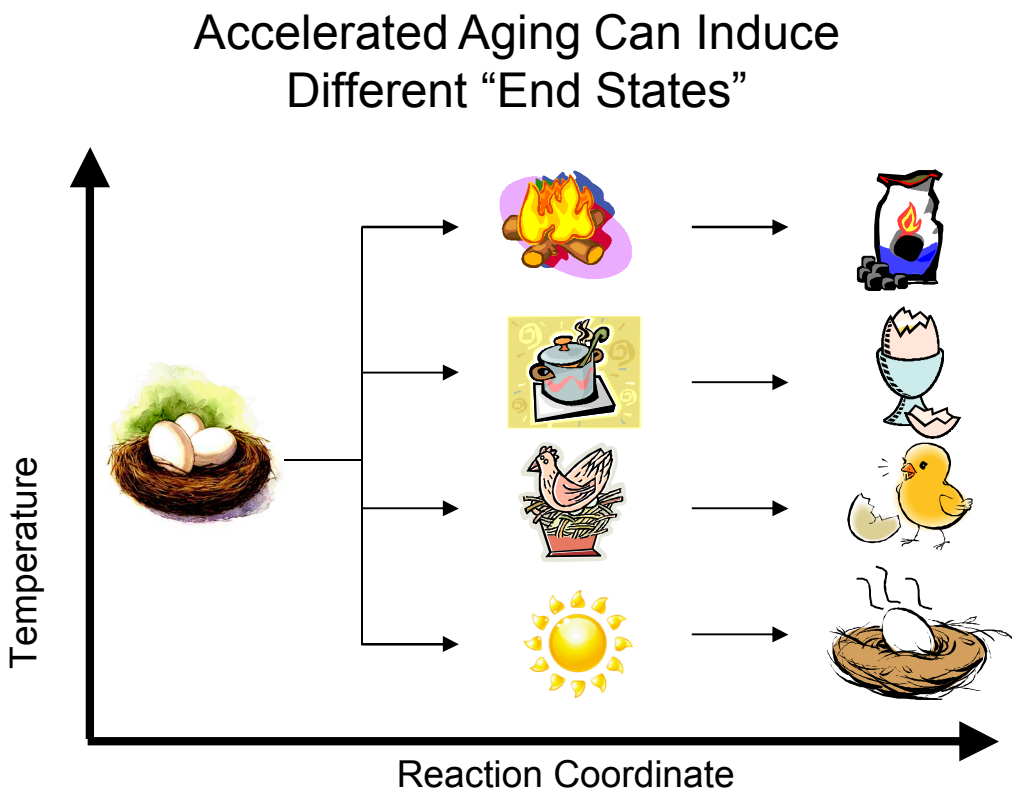


Notes: 500 drop increments, alternating inks. Only shaded vials need to be weighed before/after (calibrations)

Environmental conditioning

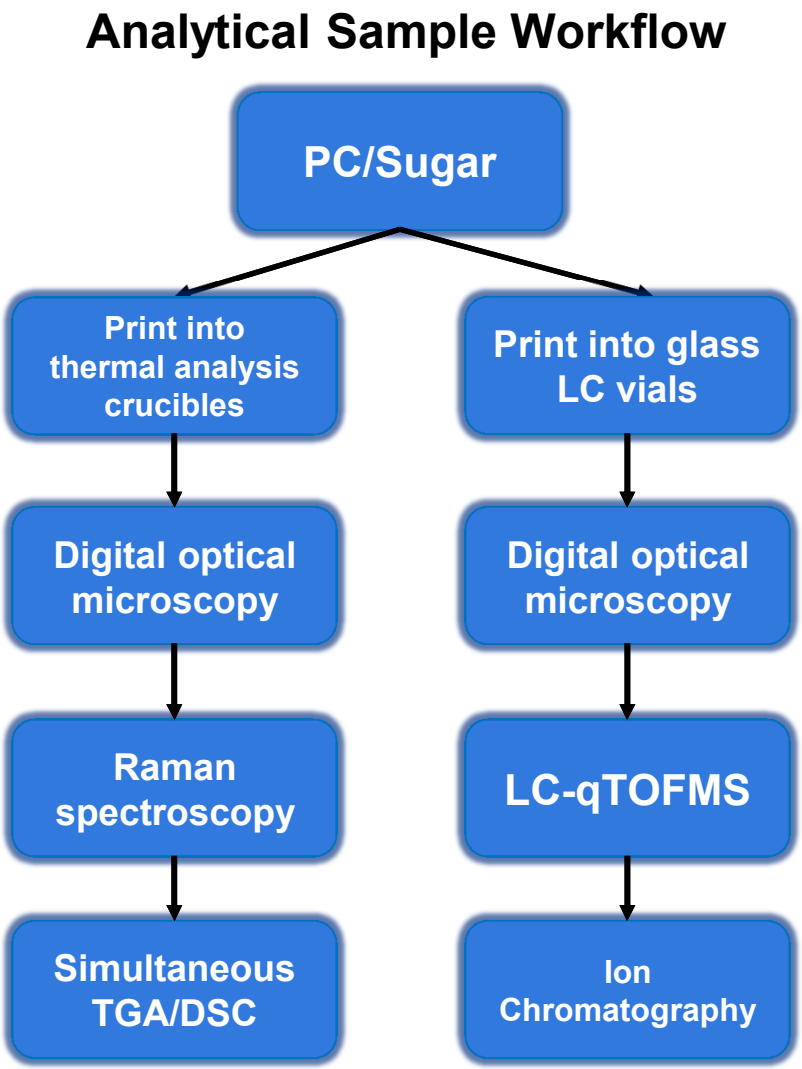
- Real HME threats are made, stored, and emplaced in real environments
- Varying some simple parameters like temperature and humidity may change some of the chemical reaction rates and/or decomposition kinetics of the materials or impurities in the materials
- There is precedence for this:
  - Accelerated aging experiments coupled with the Arrhenius equation are a common technique
  - Others have looked at effects of moisture on HME stability





Analytical Chemistry

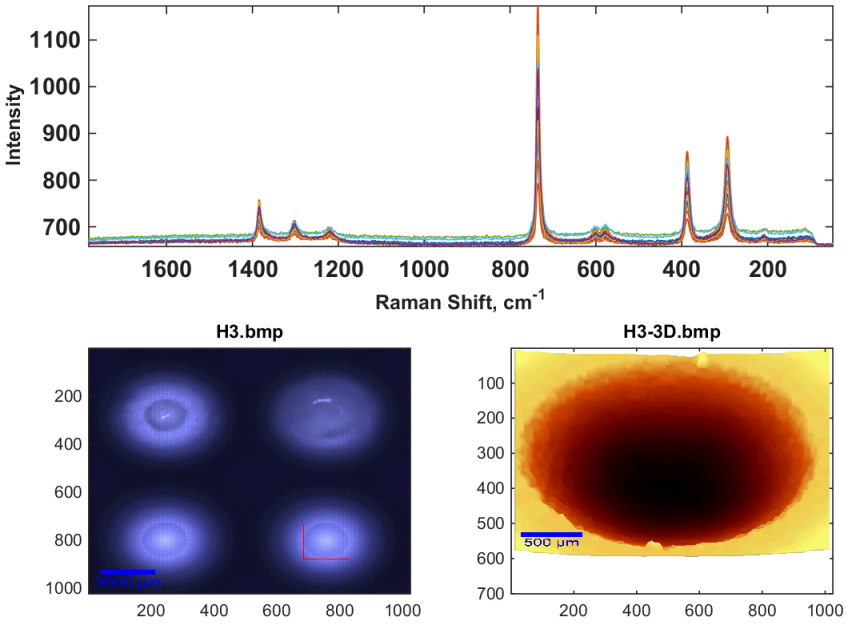
- Interested in understanding a number of physical and chemical properties of formulations including:
  - Vapor pressures
  - Degradation products
  - Impurities
  - Material lifetimes
- Plan on using a suite of analytical instrumentation including:
  - Optical Microscopy
  - Raman Spectroscopy
  - Simultaneous thermogravimetric analysis (TGA) / differential scanning calorimetry (DSC)
  - Mass Spectrometry (with LC/GC front end)
  - Ion chromatography
- Analytical methods will be more/less used depending on the materials and/or expected/found discrepancies between samples



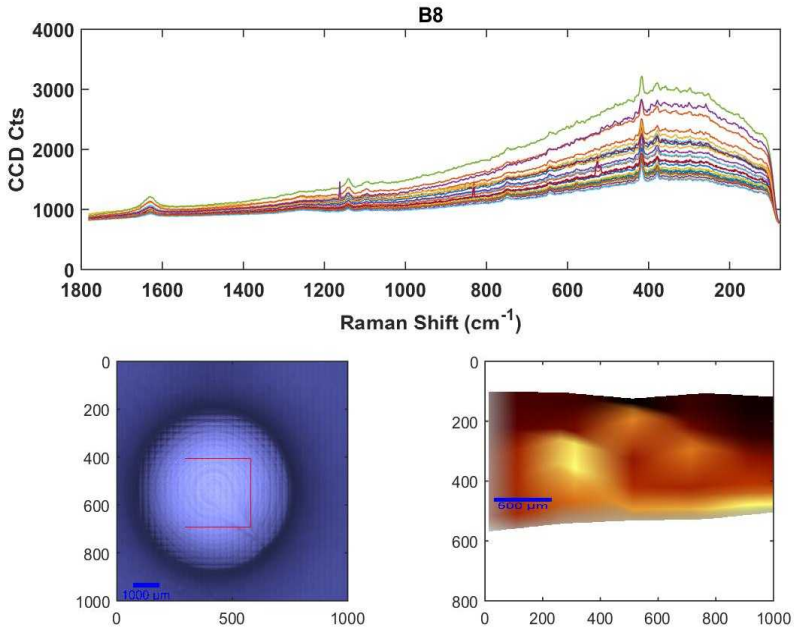
Raman Analysis

- 785 nm laser , 500 × 500 µm spatial resolution
- Pushbroom type of data collection – sweeps across wells from 5 different ‘y’ positions
- Laser auto-focuses as depth changes to ensure accurate data collection

Teflon (empty well)

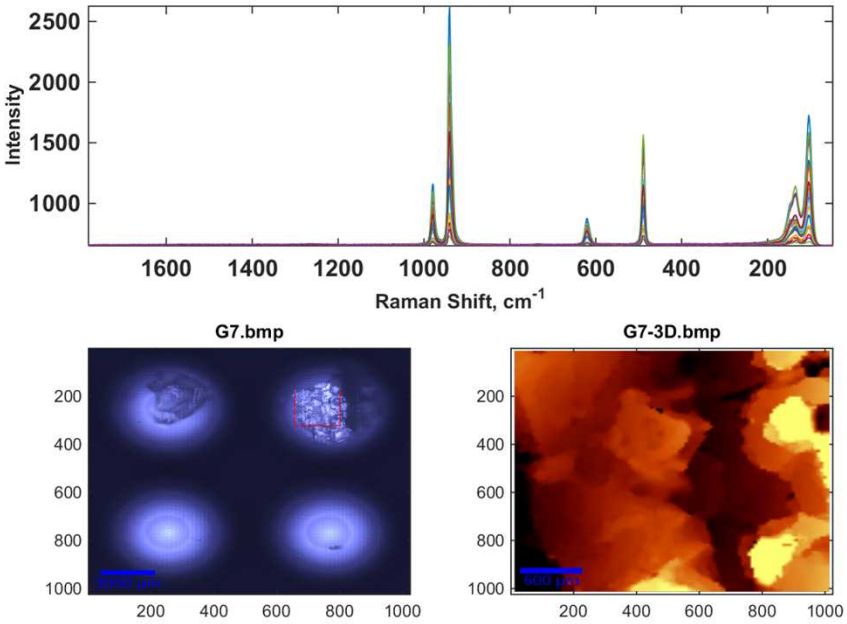


Alumina ceramic crucible (empty well)

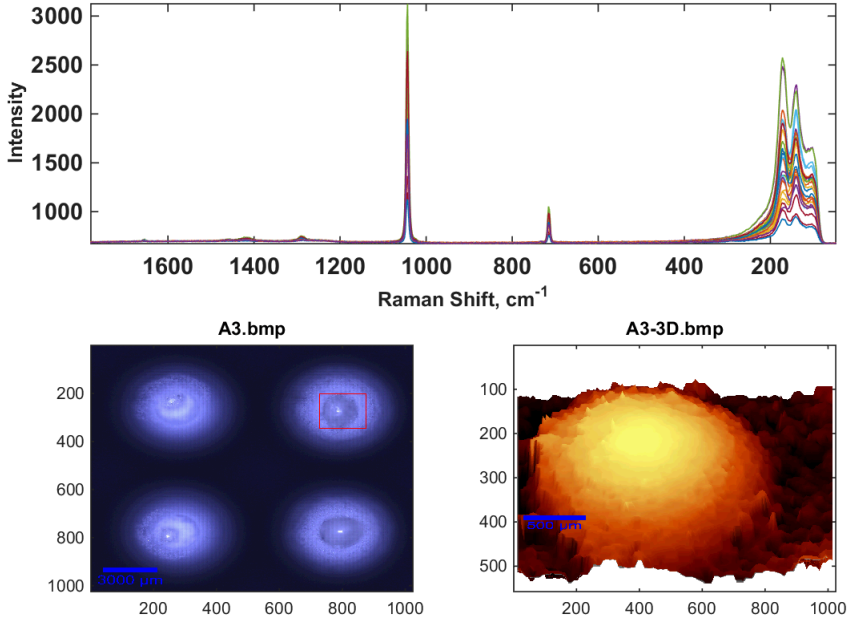


Raman Analysis - continued

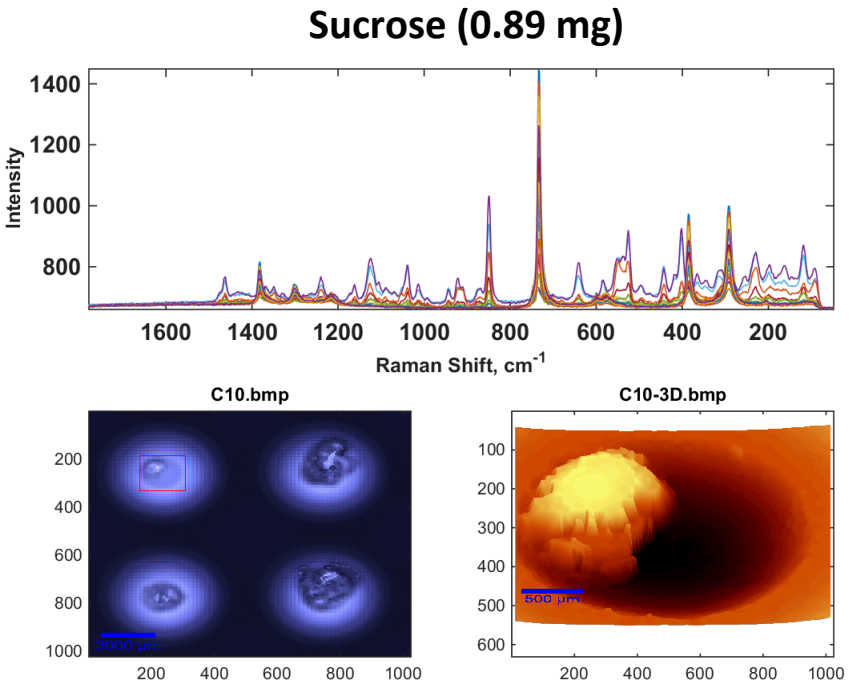
Potassium Chlorate (17.66 mg)



Ammonium Nitrate (4.97 mg)



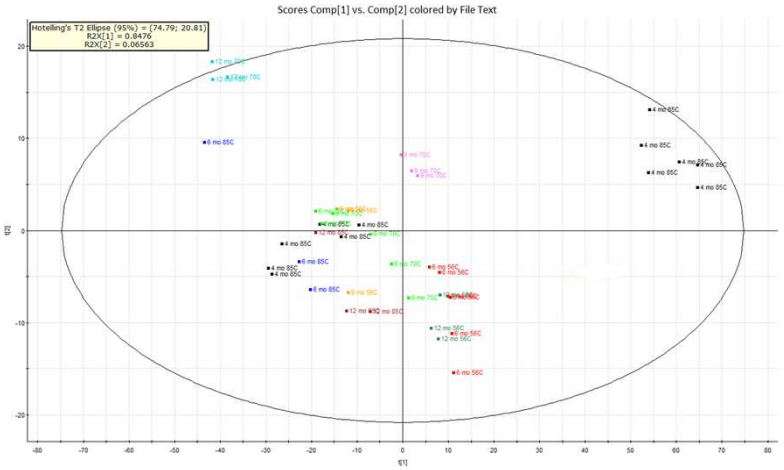
Raman Analysis - continued



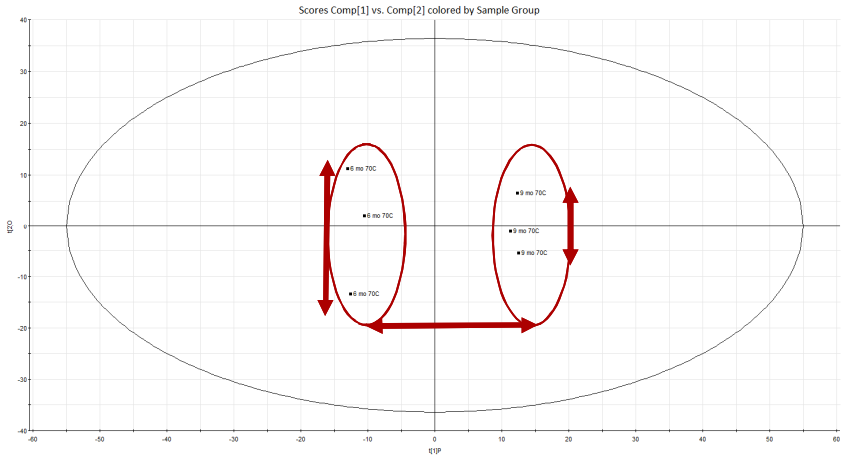
Data Analysis

- MATLAB and SIMCA-based statistical analysis software
  - Writing custom MATLAB scripts to automate pre-processing of each type of data
- Multivariate analysis including PCA and OPLS-DA
  - Find between-group and within-group differences
- End goal
  - Rapidly pre-process the different types of data
  - Combine results from various data 'streams' to produce value-added information not found from individual data sets.

Example of Scores plot generated by PCA



Example of Scores plot generated by OPLS-DA



Questions?